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Structure formation and characteristics of chromium carbide–iron–titanium cermets

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Abstract. Structure formation and properties of chromium carbide-based cermets with iron–titanium binder were investigated. Chromium carbide (50–70 wt%), Fe, and Ti (Fe : Ti ratio 4 : 1 as the binder phase) powders were milled in an attritor and a ball mill, compacted, and sintered at different temperatures and for different periods in vacuum. The microstructure, phase formation, and the composition of cermets were studied using XRD and EDS analysis and SEM. The results show that during the sintering of the Cr_3C_2–Fe–Ti composite at temperatures above 1000 °C, diffusion of chromium and carbon into the ferritic matrix and Cr_3C_2 recrystallization into the chromium ferrous dicarbide $(Cr,Fe)_{23}C_6$ and the formation of chromium solid solution in the iron matrix (Fe(Cr) take place. Titanium participates actively in the interaction process, which leads to the formation of TiC carbides even at 1200 °C. The mechanical properties (hardness, fracture toughness) and corrosion resistance in salt water were studied. Cermets sintered at lower temperature during a longer period demonstrated the best complex of mechanical properties.

Key words: chromium carbide-based cermets, structure formation, iron alloys bonded cermets, mechanical characteristics, corrosion resistance.

1. INTRODUCTION

Chromium carbide-based cermets are materials of interest in different application areas due to their unique properties. The hardness of Cr_3C_2–Ni cermets is high and they exhibit excellent corrosion, oxidation, abrasion, and erosion resistance [1–8]. The main disadvantages of these cermets are relatively low mechanical properties (transverse rupture strength (TRS), fracture toughness) because of their coarse-grained structure [9].

Chromium carbide cermets with iron as the binder can replace the expensive and toxic nickel, thus extending the application of chromium carbide materials [10–16]. However, Cr_3C_2–Fe cermets have not been used because of their high brittleness and low TRS (190 MPa), a successful solution can be achieved only at an iron content above 40 wt% [10]. When the iron content is lower, almost all of it forms a complex carbide $(Cr_{0.43},Fe_{0.37})_7C_3$ [13].

Sintering temperature and sintering time are the most important technological factors determining the structure and properties of Cr_3C_2-based cermets. A pronounced growth of carbide grains during sintering is one of the main disadvantages of Cr_3C_2-based cermets [9].

One of the objectives of this investigation was to prevent carbide grain growth in Cr_3C_2–Fe cermets by alloying them with titanium (20 wt% in Fe). The focus was on the influence of technological factors (milling method, sintering temperature, and sintering time) on the structure formation and mechanical properties of Cr_3C_2–Fe–Ti cermets.

2. MATERIALS AND EXPERIMENTAL METHODS

The chromium carbide-based composites were produced in the Laboratory of Powder Metallurgy of Tallinn University of Technology using conventional powder metallurgy technology. Chromium carbide (Cr_3C_2) and

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pure iron (Fe) and titanium (Ti) powders were used as starting materials milled in an attritor or a ball mill. The attritor and the ball mill lining were reinforced with a WC–Co alloy. To minimize contamination WC–Co balls (diameter 6 mm) were used as the milling balls. The charge ratio (ball to powder mass ratio) in the attritor was 5 : 1. The rotation speed of the impellers was 560 rpm. Kerosene was used as the milling environment, which allows adding the plasticizer (paraffin) solution during the initial stage of milling. The plasticizer forms a thin film on the powder particles, thus preventing additional access of air to the ultra-fine active powder particles. Powder mixtures with similar composition were also milled in the ball mill during 72 h. The charge ratio was 10 : 1.

The compacts (22 mm × 6 mm × 6 mm) were sintered in a furnace with graphite heaters. The compacted samples were sintered in vacuum during 30 and 60 min at 800–1470 °C, heating rate 10 °C min^{-1}. Different Cr_3C_2 contents (50, 60, and 70 wt%) and Fe : Ti ratio of 4 : 1 in the metallic binder were tested. The main focus was on cermets with 70 wt% of chromium carbide, which ensures acceptable hardness (~1200 HV) and resistance to wear (Table 1).

Phase identification of the milled powders was carried out using X-ray diffraction (XRD) methods with Cu Kα radiation (Bruker AXS D5005). The microstructure and grain size of the sintered samples were characterized using a scanning electron microscope (SEM) JEOL-840A.

Vickers hardness was determined in accordance with the standard EN ISO 6507-1 (HV_{30}). Fracture toughness was determined by the Palmqvist method. Each test point indicates the average value of five measured results [17]. The porosity of cermets was determined using an optical microscope Axiovert 25 and Buehler Omnimet software.

3. RESULTS AND DISCUSSION

3.1. Structure formation during sintering

XRD patterns of mechanically activated Cr_3C_2, Fe, and Ti powder mixtures after sintering at 800, 1000, 1200, and 1420 °C are presented in Fig. 1. As it follows from the figure, the as-milled powder mixture consists of

Table 1. Chemical composition, technological parameters, and mechanical properties of Cr_3C_2–Fe–Ti cermets

Grade	Composition, wt%			Milling device	Sint. temp, °C	Sint. time, min	Porosity, %	HV_{30}, GPa	K_{1C}, MPa·$m^{1/2}$
	Cr_3C_2	Fe	Ti						
E1-1	50	40	10	Attritor	1390	30	0.29	979±95	7.8±0.8
E2-1	60	32	8	Attritor	1450	30	0.55	995±11	4.8±0.5
E3-1	60	32	8	Ball mill	1450	30	2.01	1008±21	5.5±0.4
E4-1	70	24	6	Attritor	1420	30	0.37	1180±19	5.6±0.9
E4-2	70	24	6	Attritor	1470	30	0.84	1349±17	3.9±0.2
E4-3	70	24	6	Attritor	1420	60	0.47	1067±20	7.7±0.7
E5-1	70	24	6	Ball mill	1420	30	1.38	1274±33	5.4±0.1
E5-2	70	24	6	Ball mill	1470	30	0.15	1133±31	5.4±0.1
E5-3	70	24	6	Ball mill	1420	60	0.92	1163±6	6.0±0.4

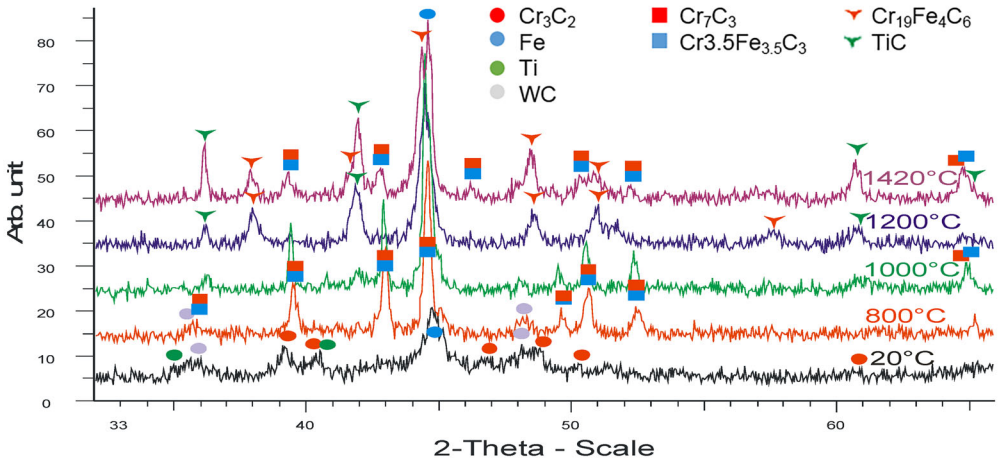

Fig. 1. X-ray diffraction pattern of the 70 wt% Cr_3C_2–Fe–Ti composite at different sintering temperatures.

three phases: Cr_3C_2, Fe, and Ti. After sintering at 800 °C for 30 min, the transformation of phases took place: additional Cr_7C_3 and $(Cr_{3.5},Fe_{3.5})C_3$ phases appeared and Cr_3C_2 disappeared. The presence of the Cr_7C_3 phase may be indicative of a low stability of Cr_3C_2 at high temperatures. In the Fe matrix Cr_3C_2 dissolves and forms a complex carbide $(Cr_{3.5},Fe_{3.5})C_3$ and a solid solution of Cr in iron Fe(Cr). After sintering at 1000 °C, additional TiC lines appeared. This means that Ti reacts with carbon and forms TiC already at a temperature below 1000 °C.

Significant changes in the XRD pattern (see Fig. 1) took place after sintering at 1200 °C during 30 min. The reason probably was the formation of liquid eutectic at this temperature. A liquid phase was formed and a new phase $(Cr,Fe)_{23}C_6$ appeared (Fig. 1). The exact content of the phase was $(Cr_{18.93},Fe_{4.07})C_6$. During the sintering at 1420 °C for 30 min, no remarkable changes in the XRD diagram were noticed. The composite consists of three main phases: chromium ferrous complex carbide $(Cr,Fe)_{23}C_6$, solid solution Fe(Cr), and titanium carbide TiC. The reaction during the sintering of the alloy can be described as follows:

$$Cr_3C_2 + Fe + Ti \rightarrow (Cr,Fe)_{23}C_6 + TiC + Fe(Cr).$$

Also the EDS analysis confirmed this. The dark grey region in Fig. 2a is dicarbide $(Cr,Fe)_{23}C_6$. The light grey

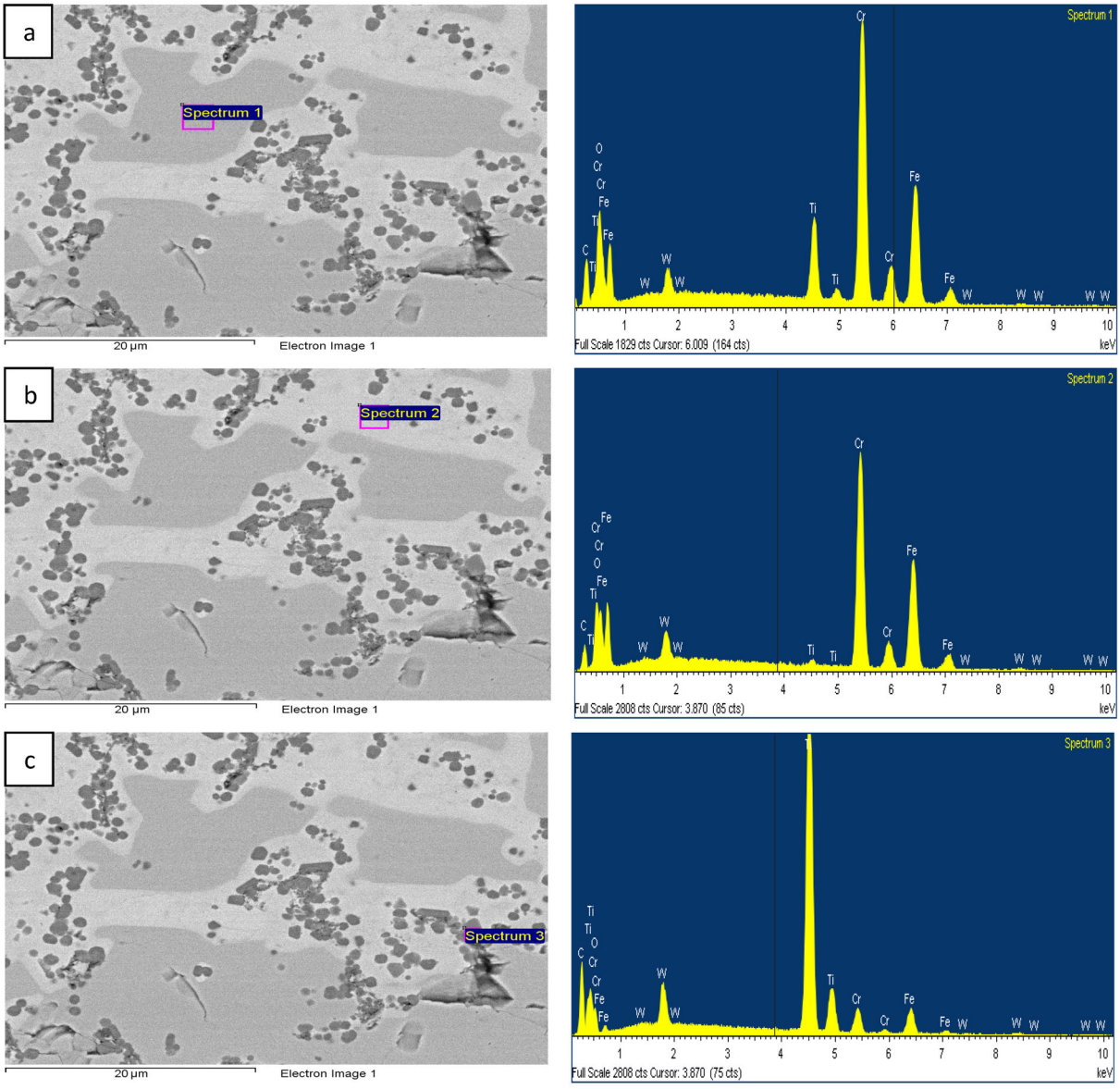

Fig. 2. Results of the EDS analysis at three points (spectra 1, 2, and 3; 1420 °C): (a) $(Cr_{19},Fe_4)C_6$; (b) Fe(Cr); (c) TiC.

region (Fig. 2b) is the solid solution of chromium in the iron matrix. The content of Cr is approximately 33 wt% in Fe. Ultrafine (below 1 μm) black near-spherical particles are TiC grains (Fig. 2c). We can see that dispersed TiC grains precipitate in the metallic Fe(Cr) phase.

3.2. Microstructure

The formation of microstructure during the sintering of Cr_3C_2–Fe–Ti cermets was examined using SEM. The results are given in Fig. 3. The carbide grain size in the cermets is determined by sintering parameters and by the particle size of the powder. The rapid grain growth during solid and liquid phase sintering is one of the main disadvantages of chromium carbide-based cermets [9]. As seen in Fig. 3b, the cermets sintered at 1000 °C during 30 min have fine particles: the average carbide grain size is below 1 μm. In these cermets no carbide grain growth can be observed as compared to the initial particle size (Fig. 3a). A remarkable carbide grain growth occurs in alloys sintered at 1200 °C (Fig. 3c). The average carbide grain size is 2–3 μm. The structure contains many pores. The high porosity of these cermets is caused by the low liquid phase content at this sintering temperature.

The microstructure of the cermets sintered at 1420 °C has coarse $(Cr,Fe)_{23}C_6$ carbide grains, making the cermets weak and brittle (Fig. 3d). The in situ synthesized titanium carbide grains are fine-grained and are situated mainly in the Fe(Cr) solid solution and between the carbide grains.

An alternative approach to reduce the grain size of chromium carbide-based cermets is using additions of TiC as a grain size inhibitor (compare Fig. 4b and c). The grain size of Cr_3C_2–Fe–Ti and Cr_3C_2–TiC–Fe cermets is similar.

3.3. Mechanical properties

The mechanical properties of Cr_3C_2–Fe–Ti cermets are summarized in Table 1. The properties of sintered cermets depend on their composition and microstructure. A coarse

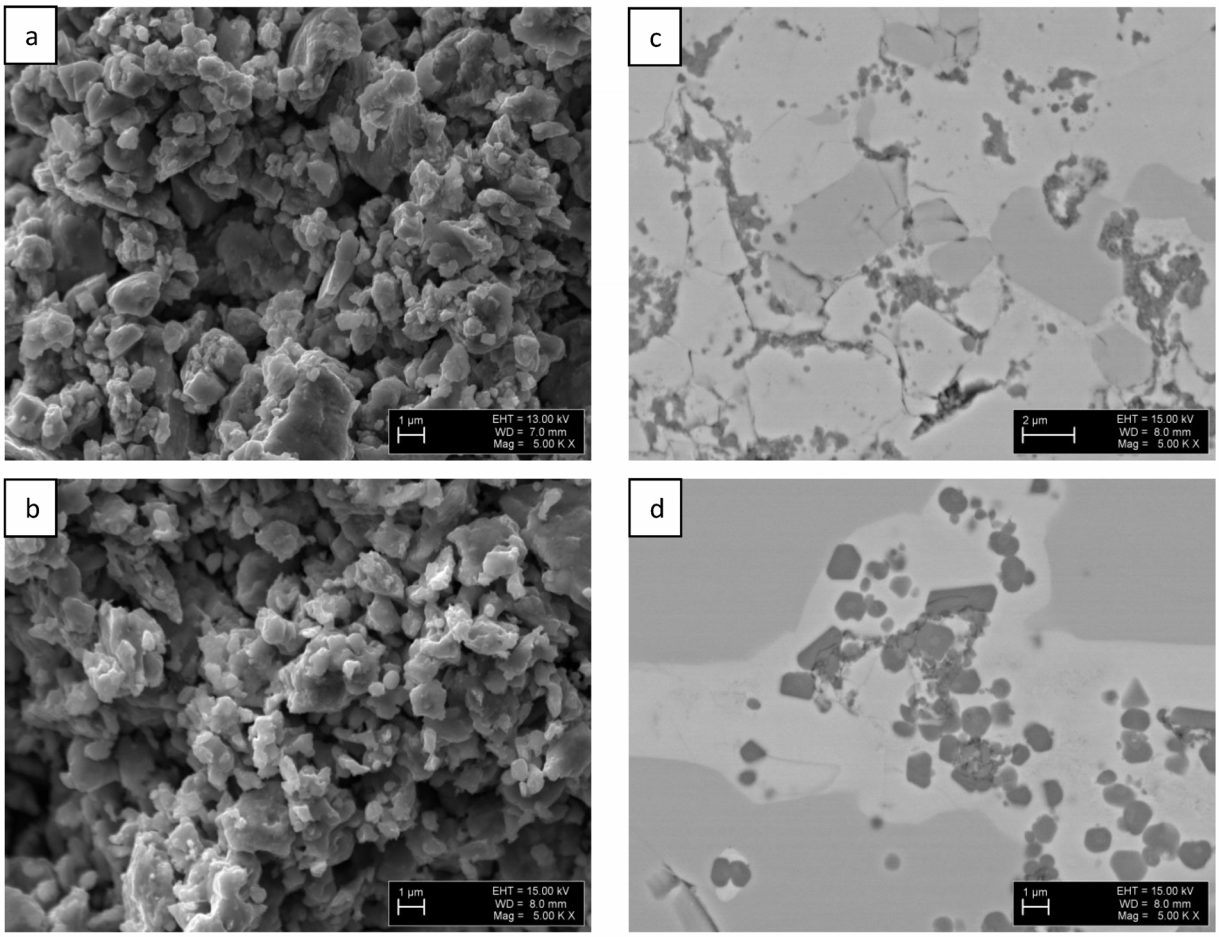

Fig. 3. SEM images of Cr_3C_2–Fe–Ti composite structure formation sintered at different temperatures: (a) as-milled powder mixture; (b), (c), (d) sintered at temperatures 1000, 1200, and 1420 °C, respectively.

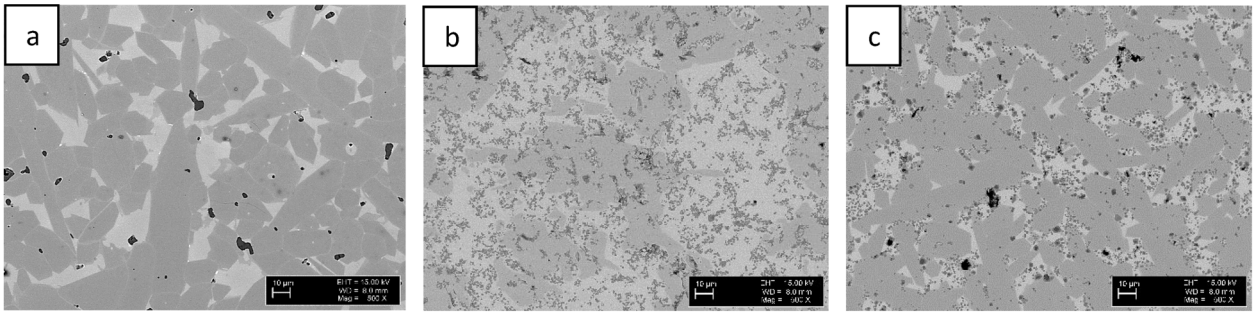

Fig. 4. SEM images of Cr_3C_2–Fe (a), Cr_3C_2–Fe–Ti (b), and Cr_3C_2–TiC–Fe (c).

microstructure of chromium carbides is the reason of moderate mechanical properties (fracture toughness). Like most ceramics, chromium carbides are intrinsically brittle. On the atomic level, this brittleness of carbides is related to their strong hybrid ionic–covalent bonds, which prevent plastic deformation similar to that encountered in ductile metals [15].

The hardness of the cermets depends mainly on the Cr_3C_2 content in the initial powder mixture, being between 980 and 1350 HV. This demonstrates that the hardness increases with the increasing carbide content due to an increase in the fraction of the hard carbide phase. Hardness is practically independent of the milling device (attritor or ball mill) used. Fracture toughness of chromium carbide-based cermets is comparatively low (4–8 MPa·$m^{1/2}$). The lower the sintering temperature, the smaller is the carbide grain size and the higher is the fracture toughness.

Salt corrosion tests of Cr_3C_2–Fe–Ti cermets showed that they were resistant to corrosion in 3.5% NaCl water solution at room temperature for 72 h. Corrosion resistance did not depend on the composition of cermets and technological parameters used.

4. CONCLUSIONS

Results obtained from the investigation of the influence of the composition of cermets and technological factors on the structure formation and mechanical characteristics of Cr_3C_2–Fe–Ti cermets provide basis for the following conclusions:

- During the sintering of the Cr_3C_2–Fe–Ti composite at a temperature above 1000 °C, diffusion of chromium and carbon into the ferritic matrix, Cr_3C_2 recrystallization into chromium ferrous complex carbide $(Cr,Fe)_{23}C_6$, and formation of chromium solid solution in the iron matrix Fe(Cr) take place. Titanium participates actively in the interaction process, which leads to the formation of TiC carbides even at 1200 °C.
- There is no significant difference in the structure and mechanical properties of composites milled in an attritor or in a ball mill. At the same time, sintering temperature and time affect the structure and properties of the cermets.
- Cermets sintered at lower temperature during a longer time demonstrated the best complex of hardness–toughness properties.

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Kroomkarbiidkermiste struktuuri moodustumine ja karakteristikud

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Käesolevas töös uuriti kroomkarbiidi baasil kermiste omadusi ja struktuuri moodustumise protsesse. Kroomkarbiid (50–70 massiprotsenti), raud (Fe) ja titaan (Ti) (Fe : Ti = 4 : 1) jahvatati atriitoris ning kuulveskis, pressiti ja seejärel paagutati, kasutades erinevaid režiime (temperatuur, kestus). Struktuuri moodustumise protsesside, faasilise ja keemilise koostise uurimiseks kasutati skaneerivat elektronmikroskoopiat ning röntgendifraktsioonanalüüsi. Uuringute tulemusena selgus, et vaakumpaagutamisel toimuvad alljärgnevad protsessid: kroom ja süsinik difundeeruvad ferriitsesse sideainesse ning Cr_3C_2 rekristalliseerub, moodustades rauaga kaksikkarbiidi $(Cr,Fe)_{23}C_6$. Moodustub raua-kroomi tardlahus Fe(Cr), temperatuuridel alates 1200 °C tekivad peeneteralised titaankarbiidi osakesed. Määrati kermiste mehaanilised omadused (kõvadus, purunemissitkus), samuti hinnati korrosioonikindlust NaCl vesilahuses (3,5% NaCl). Parimate mehaaniliste omadustega on kermised, mis on paagutatud võimalikult madalal temperatuuril pikema aja jooksul.